

Ti³⁺ IN METEORITIC AND SYNTHETIC HIBONITE: A NEW OXYGEN BAROMETER: D. Live^{1,2}, J.R. Beckett², F-D. Tsay¹, L. Grossman³, and E. Stolper². ¹Jet Propulsion Laboratory, Caltech, Pasadena, CA 91109. ²Div. Geol. Planet. Sci., Caltech, Pasadena, CA 91125. ³Dept. of Geophys. Sci., U. Chicago, Chicago, IL 60637.

Introduction. Mineral compositions in Ca-, Al-rich inclusions (CAIs) from chondritic meteorites reflect conditions in the early solar nebula. Precise determinations of the f_{O_2} levels that they record would provide critical information on the composition of the nebular gas, since f_{O_2} is sensitive to proportions of H, C and O. Despite the importance of f_{O_2} for understanding nebular conditions, there have been few quantitative estimates of the f_{O_2} levels recorded by CAIs (1-4); qualitatively, however, it is clear that there are variations of many orders of magnitude, even within individual inclusions (1).

We report the first direct determination of Ti³⁺ in meteoritic and synthetic hibonite. We used electron spin resonance (ESR) spectroscopy, a sensitive and widely used technique for analyzing transition metal ions (5), to (a) unequivocally detect Ti³⁺ in hibonite, (b) characterize Ti³⁺ sites, (c) quantify concentrations of Ti³⁺, (d) define relationships between Ti³⁺/Ti⁴⁺ and f_{O_2} and (e) estimate the f_{O_2} indicated for hibonite from inclusion SH-7 (6) in Murchison.

Samples. Four synthetic hibonite compositions described by (4) were examined. BA corresponds to the composition of average core hibonite in the Blue Angel inclusion from Murchison (7), BA-V to BA with no V, BA-VFC to BA with no V, Fe or Cr and All to the average composition of orange hibonite from inclusion CG-11 of Allende (8). In addition, two samples of natural hibonite, a single grain (SH-7Hib1) weighing 37 μ g and 25 chips (SH-7Hib2) weighing a total of 135 μ g, from SH-7 were examined. Bulk composition BA-V is very close to the average composition of hibonite in SH-7, but with lower Ti (2.5 vs. 3.0 wt%).

ESR Spectra: Ti³⁺ in Hibonite. At room temperature, an ESR signal centered at $g = 1.96$ was observed for SH-7, consistent with a d^1 ion such as Ti³⁺ (5). The intensity of the signal is an order of magnitude larger than can be accounted for by any other transition metal ions in the sample. ESR spectra of synthetic hibonites equilibrated at selected temperatures and f_{O_2} 's were also examined. As shown in Fig. 1, intensity of the signal centered at $g = 1.96$ increases with decreasing f_{O_2} . The resonance is present for BA-VFC, in which Ti is the only transition element, at approximately the same level as in the other BA compositions. These observations support the assignment of the ESR signal at $g = 1.96$ to Ti³⁺ in natural and synthetic hibonite.

The ESR signal for Ti³⁺ is readily observed at room temperature, indicating that Ti³⁺ is in a distorted site (5). The principal values of the g tensor, $g_{\parallel} = 1.997$ and $g_{\perp} = 1.951$, were determined from polycrystalline synthetic hibonite, indicating an axially symmetric site. Based on ESR spectra of the single crystal SH-7Hib1 taken at different angles relative to the magnetic field, g_{\parallel} is parallel to the crystallographic c -axis while g_{\perp} is in the ab plane. The only site in the hibonite structure (9) consistent with this arrangement is the 5-coordinated Al-site. No additional signals were detected in spectra on SH-7Hib1 taken at temperatures as low as 4K or on BA-VFC hibonite at 77K. Intensity varied in a normal manner (5) with T for these samples. Since ESR signals for Ti³⁺ in symmetric octahedral sites of the structurally very similar β -alumina were readily detected at 150K (10), Ti³⁺ substituting in other Al-sites in hibonite probably would have been observable if present. Thus, we conclude that Ti³⁺ is dominantly present in the 5-coordinated site and that essentially all Ti³⁺ in hibonite was detected.

Ti³⁺ Concentrations and Oxygen Fugacity. The concentration of Ti³⁺ was determined from ESR spectra by double integrating over the signal centered at $g = 1.96$, normalized to constant operating conditions and sample weight. Only small concentrations of Ti³⁺ are present in synthetic and meteoritic hibonite. SH-7Hib1 has 0.12 wt% Ti³⁺ while SH-7Hib2 has 0.17 wt%. Thus, only 4-6 % of all Ti in the Murchison samples is Ti³⁺. For synthetic blue hibonite, there is 0.01-0.24 wt%,

corresponding to 0.5-10% of Ti as Ti³⁺. Most electron probe analyses of meteoritic hibonite (7,8) are consistent with negligible Ti³⁺ contents, but it is unlikely that the microprobe is either sufficiently accurate or precise to detect such small amounts of Ti³⁺. The concentration of Ti³⁺ in orange synthetic hibonite is less than the detection limit of (<0.1% of total Ti for those samples), supporting the contention of (4) that the blue-to-orange transition is related to oxidation of Ti³⁺.

In Fig. 2, $\log(Ti^{3+}/Ti^{4+})$ for synthetic hibonite is plotted as a function of the difference between the $\log f_{O_2}$ of the experiment and that of a gas of solar composition at the same temperature. At constant f_{O_2} , Ti^{3+}/Ti^{4+} increases with increasing total Ti and decreasing V. The latter suggests that V³⁺ competes with Ti³⁺ for the 5-coordinated Al-site (4). At constant T and Ti^{3+}/Ti^{4+} in hibonite, the difference in $\log f_{O_2}$ between that of a solar gas and All or BA-V experiments is consistent with being a constant.

Under oxidizing conditions (region of solid lines in Fig. 2), Ti^{3+}/Ti^{4+} is proportional to $f_{O_2}^{-1/6}$. This is consistent with reduction of Ti⁴⁺ by trapping of electrons according to $2Ti^{4+} + V_0^x = 2Ti^{3+} + V_0^{2+}$, where V_0^x and V_0^{2+} are, respectively, neutral and doubly charged oxygen vacancies. Under more reducing conditions, Ti^{3+}/Ti^{4+} in synthetic hibonite is generally below that expected from higher f_{O_2} experiments. Deviations from a line of slope -1/6 may be due to precipitation of other phases in hibonite, difficulty in quenching and/or a change in the defect mechanism.

$\log(Ti^{3+}/Ti^{4+})$ equals -1.39 for SH-7Hib1 and -1.22 for SH-7Hib2. Assuming that an extension of the -1/6 line for BA-V is approximately correct for SH-7, we obtain an upper limit on f_{O_2} approximately 3-4 orders of magnitude more oxidizing than a solar gas. If a line with a shallower slope is more appropriate, then more reducing, possibly solar, f_{O_2} 's would be predicted. The upper limit is comparable to estimates of f_{O_2} based on the intensity of color in Blue Angel hibonite (4) and on geochemical modelling (3) of CAI bulk compositions. It is more oxidizing than f_{O_2} levels estimated from fassaite in CAIs from Allende (2).

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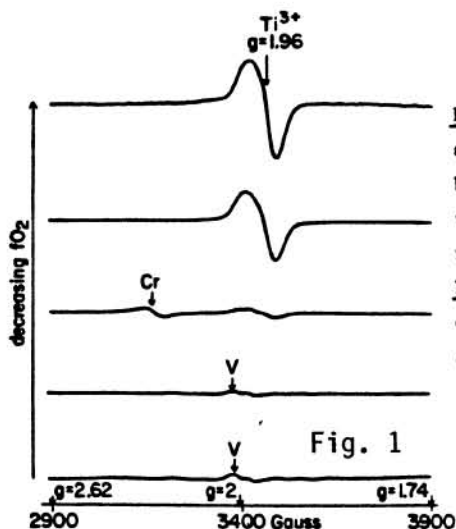


Fig. 1: ESR spectra of several synthetic hibonites presented as the 1st derivative of the absorption signal. Fig. 2: $\log(Ti^{3+}/Ti^{4+})$ of synthetic hibonites as a function of $\log(f_{O_2}^{EXPT}/f_{O_2}^{SOLAR})$.

